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Description	

# Unusually large absolute Raman scattering cross section of hydrogen vibrations on Si(111)

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We have measured the absolute Raman scattering cross section of the terrace vibration mode of silicene-monohydride on a Si(111) surface that was prepared by chemical etching in a  $\text{NH}_4\text{F}$  solution. The measured cross section at the incident wavelength of  $4880 \text{ \AA}$  is  $(d\sigma_{zz}/d\Omega) = (8.37 \pm 0.32) \times 10^{-28} \text{ cm}^2/(\text{sr line Si-H bond})$ . It is about 74 times the cross section of the symmetric stretching mode of the gaseous  $\text{SiH}_4$  molecule. The measured excitation profile of the cross section in the range of  $\lambda_{\text{in}} = 4579\text{--}5145 \text{ \AA}$  has a  $\omega^4$  dependence indicating that there is no resonant enhancement of the cross section. We estimate that the Raman transition dipole matrix elements are about three times larger for the Si(111)/H monolayer system than for the free  $\text{SiH}_4$  molecule.

## I. INTRODUCTION

Raman scattering is a powerful tool for investigations of molecular vibrations. However, its surface sensitivity is appreciably lower compared with infrared absorption spectroscopy and electron-energy-loss spectroscopy (EELS). Thus it has been extremely difficult to detect weak Raman scattered light from a monolayer adsorbed on solid surfaces, except in cases where surface-enhanced Raman scattering (SERS) occurs<sup>1</sup> or electronic resonances enhance Raman intensities.<sup>2,3</sup> Only a few examples of successful observation of "unenhanced" Raman scattering from a monolayer have been reported; e.g., nitrobenzene, pyridine, and benzene on Ag and Ni by Campion and co-workers<sup>4-6</sup> and nitrobenzene on Ni by Chou *et al.*<sup>7</sup>

Recently Hines *et al.*<sup>8</sup> have observed the Raman spectra of the Si-H stretching vibrations on a H-terminated Si(111) surface with an unusually high signal-to-noise ratio. Their results suggest that the Raman scattering cross section of the Si-H stretching mode is unusually large. There are only a few reports on the SERS effect on semiconductor surfaces,<sup>9-11</sup> and in particular no report of SERS on Si surfaces. Thus the strong Raman scattering by less than a monolayer of H on Si observed by Hines *et al.* is very intriguing. The question is what enhances the Raman intensity so much in this sample system.

As a first step toward understanding the mechanism that causes the unusually large Raman signal from the Si-H system, we have measured the absolute Raman scattering cross section of this mode. We then examined various possible enhancement mechanisms.

## II. EXPERIMENT

The sample substrates were B-doped *p*-type Si(111) with resistivity  $\rho = 7\text{--}7.5 \text{ \Omega cm}$  and Si(100) with  $\rho = 1.3\text{--}1.7 \text{ \Omega cm}$ . The substrates were prepared in a clean room by the following steps using high-grade reagents and purified containers suitable for silicon device processing: (1) Two cycles of cleaning in a hot solution of 97%  $\text{H}_2\text{SO}_4$ :30%  $\text{H}_2\text{O}_2 = 4:1$  (5 min) and rinsing with high-purity deionized (DI) water (4 min). (2) Etching in a 1% HF solution and rinsing with DI

water (4 min). (3) Reoxidizing in a hot solution of 97%  $\text{H}_2\text{SO}_4$ :30%  $\text{H}_2\text{O}_2 = 4:1$  (5 min), and rinsing with DI water (4 min). (4) Etching in a 40%  $\text{NH}_4\text{F}$  solution (90 s) and rinsing with DI water (4 min). (5) Reoxidizing in a hot solution of 97%  $\text{H}_2\text{SO}_4$ :30%  $\text{H}_2\text{O}_2 = 4:1$  (5 min) and rinsing with DI water (6 min). (6) Etching in a 40%  $\text{NH}_4\text{F}$  solution (3 min). (7) Rinsing with DI water (10 s) and venting with dry  $\text{N}_2$  gas.

For one of the Si(111) substrates, a different sample preparation method was also used: etching in a 1% HF solution (3 min) instead of the last etching process (6) in a 40%  $\text{NH}_4\text{F}$  solution (3 min).

Studies by scanning tunneling microscope (STM) (Refs. 12-14) and multiple internal reflection absorption spectroscopy (MIRAS) (Refs. 15 and 16) have shown that the surface morphology and the surface-adsorbed species after etching processes depend on the crystal orientation of the Si surface and the pH of the HF solution. These results can be explained by the extremely low etching rate along the [111] direction by a high-pH HF solution. From the results reported in Refs. 12-16, we can say with fair certainty that the three kinds of samples we prepared have the surface properties described below.

**Sample A:** Etched Si(111) in a 40%  $\text{NH}_4\text{F}$  solution (pH of 7.8) in the last stage of sample preparation. This sample has an atomically flat and ideally monohydride-terminated (111) surface.

**Sample B:** Etched Si(111) in a 1% HF solution (pH of 2) in the last stage of sample preparation. This surface is uniformly covered with atomic scale roughness. There are dihydrides and trihydrides in addition to monohydrides on the surface.

**Sample C:** Etched Si(100) in a 40%  $\text{NH}_4\text{F}$  solution (pH of 7.8) in the last stage of sample preparation. This surface is rough like sample B and has etch pits. Various species, i.e., monohydrides, dihydrides, and trihydrides, exist on the surface.

The Raman spectra were measured immediately after the sample preparation, using an argon-ion laser as the incident light source. The incident wavelengths and the incident power were as follows: For sample A,  $4579 \text{ \AA}$  (83 mW),  $4765 \text{ \AA}$  (265-290 mW),  $4880 \text{ \AA}$  (400-408 mW), and  $5145$

Å (397–413 mW); and for samples *B* and *C*, 4880 Å (400 mW). The incident angle was 60° from the surface normal, and the polarization was parallel to the plane of incidence (*p* polarized). To lower the power density on the sample surface, the laser beam was focused with a cylindrical lens to form an elliptical spot of roughly 2×3 mm on the surface. The scattered light was collected in a direction 60° from the surface normal in a plane rotated by 20° from the incident plane. The solid angle of collection was  $\Delta\Omega = 2.84 \times 10^{-2}$  sr. The spectrometer is a Jobin-Yvon U-1000 double monochromator equipped with a Hamamatsu R649 photomultiplier tube. The absolute sensitivity of this spectrometer system  $\eta_{\text{sys}}$  has been calibrated as a function of wavelength and polarization by using a standard halogen lamp.<sup>17</sup> Thus the observed photon counting rate can be directly converted to absolute intensity. The cross section of the Si-H stretching vibration mode at  $\sim 2085 \text{ cm}^{-1}$  was measured in air at room temperature. To suppress the Raman scattered background due to the atmospheric  $\text{N}_2$  centered at  $\sim 2330 \text{ cm}^{-1}$ , argon gas was blown at the sample surface.

### III. ANALYSIS OF THE RAMAN CROSS SECTION OF ADSORBED MOLECULES

In this section we present the necessary formulas for calculations of the absolute Raman scattering cross section of adsorbed molecules. To obtain the absolute Raman cross section of surface-adsorbed molecules that can be compared with that of the isolated gaseous molecules, it is necessary to account for the effects of the presence of the substrate on the propagation of the incident and scattered light. We consider the Raman scattering process by surface-adsorbed molecules in three steps: (1) Generation of the local macroscopic electric field at the molecular site by the incident light. (2) Generation of the Raman dipole by the local field through the Raman tensor. (3) Propagation of the scattered light from the Raman dipole. This approach to the Raman scattering process by surface-adsorbed molecules has been described in detail by Sakamoto, Mizutani, and Ushioda.<sup>17</sup> We follow their analysis for the absolute cross section.

To analyze the specific sample configuration at hand, we adopt the three layered dielectric model that was used by Hines *et al.*<sup>8</sup> In this model the three layers consist of a semi-infinite Si substrate, an infinitely thin Si-H adsorbate layer, and a semi-infinite vacuum above. The adsorbate layer is assumed to have an isotropic real dielectric constant  $\epsilon_{\text{ads}}$ . All interfaces are assumed to be flat.

From Eq. (9) of Ref. 17 the Raman scattering intensity from an adsorbed molecule can be expressed by

$$I^{\text{out}} = \left(\frac{\omega_s}{c}\right)^4 \left(\frac{\epsilon_n(\omega_s)}{\epsilon_n(\omega_{\text{in}})}\right)^{1/2} \frac{I^{\text{in}}}{A_{\text{beam}}} \times |\mathbf{e}^{\text{out}} \underline{A}^T(\theta_s, \phi_s, \omega_s) \alpha^L \underline{A}(\theta_{\text{in}}, \phi_{\text{in}}, \omega_{\text{in}}) \mathbf{e}^{\text{in}}|^2, \quad (1)$$

where the symbols are defined as follows:  $I^{\text{out}}$  is the Raman scattering intensity per unit solid angle.  $I^{\text{in}}$  and  $A_{\text{beam}}$  are the total intensity and the illuminated area by the incident light, respectively.  $c$  is the speed of light in vacuum.  $\omega_{\text{in}}$  and  $\omega_s$  are the frequencies of the incident and scattered light, respectively.  $\epsilon_n$  is the dielectric constant of the top layer that is vacuum in our system. Thus  $[\epsilon_n(\omega_s)/\epsilon_n(\omega_{\text{in}})]^{1/2}$  becomes

unity.  $\mathbf{e}^{\text{in}}$  and  $\mathbf{e}^{\text{out}}$  are the incident and scattered polarization vectors, respectively. The angles  $\theta_j$  and  $\phi_j$  ( $j = \text{in or s}$ ) are the directions of the incident and scattered light.  $\alpha^L$  is the 3×3 Raman tensor of the scattering molecule. All Si-H bonds of the ideal Si(111) surface are directed along the  $z$  axis defined along the surface normal. Since a Si-H bond can be regarded as an isolated diatomic molecule, the Raman tensor of a Si-H bond takes the form

$$\alpha^L = \alpha_{zz}^L \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (2)$$

by symmetry.  $\delta$  is the bond anisotropy defined by the ratio of the molecular polarizabilities perpendicular and parallel to the bond axis. Hines *et al.*<sup>8</sup> have already determined  $\delta$  of the Si-H bond on Si(111) by measuring the polarization dependence of the Raman intensity. We use their value of  $\delta = 0.263$  for the present analysis.  $\underline{A}$  is the matrix that describes the propagation of the incident wave near the substrate surface and determines the incident local field in the adsorbate layer. This matrix  $\underline{A}$  consists of the electromagnetic Green's function of a layered structure that is described in detail in Ref. 18.  $\underline{A}^T$  is the transpose of  $\underline{A}$ .

In actual Raman measurements, experimental parameters such as the sensitivity of the spectrometer system ( $\eta_{\text{sys}}$ ) and the solid angle of collection ( $\Delta\Omega$ ) enter the observed Raman intensity. To include these experimental parameters, we use the following equation derived from Eq. (1):

$$N_{\text{obs}} = \eta_{\text{sys}} \Delta\Omega \rho_s \frac{\omega_s^3 \omega_{\text{in}}}{c^4} |\mathbf{e}^{\text{out}} \underline{A}^T \alpha^L \underline{A} \mathbf{e}^{\text{in}}|^2 N_{\text{in}} = \eta_{\text{sys}} \Delta\Omega \rho_s \left(\frac{d\sigma_{zz}}{d\Omega}\right) \gamma N_{\text{in}}, \quad (3)$$

where

$$\left(\frac{d\sigma_{zz}}{d\Omega}\right) \equiv \frac{\omega_s^3 \omega_{\text{in}}}{c^4} |\alpha_{zz}^L|^2, \quad (4)$$

$$\gamma = \left| \mathbf{e}^{\text{out}} \underline{A}^T \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & 1 \end{pmatrix} \underline{A} \mathbf{e}^{\text{in}} \right|^2. \quad (5)$$

The symbols in Eq. (3) are defined as follows:  $N_{\text{obs}}$  is the observed total photon number of Raman scattered light for a given vibrational mode.  $N_{\text{in}}$  is the total number of incident photons.  $\rho_s$  is the surface density of the Si-H bonds. Assuming that the Si(111) surface is perfectly terminated by hydrogen monohydride, the surface density  $\rho_s$  is equal to that of the Si atoms on Si(111), which is  $7.83 \times 10^{14} \text{ cm}^{-2}$ .  $(d\sigma_{zz}/d\Omega)$  is the quantum Raman scattering cross section defined as the ratio of the number of scattered photons per Si-H bond to the number of incident photons per unit area. The unit of the cross section is  $\text{cm}^2/(\text{sr line Si-H bond})$ .  $\gamma$  is the correction factor that arises from the effect of the local electric field. For the calculation of  $\gamma$  we use the dielectric constant of bulk Si (Ref. 19) and the dielectric constant of the adsorbate layer ( $\epsilon_{\text{ads}} = 3.78$ ) that was obtained by Hines

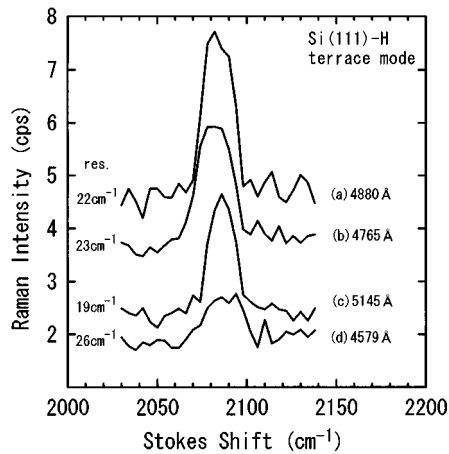


FIG. 1. Raman spectra of the terrace vibration mode of monohydride on Si(111) etched in a  $\text{NH}_4\text{F}$  solution for different incident laser wavelengths. (a) Incident power  $I_{\text{in}}=408$  mW, accumulation time/point  $T_{\text{acc}}=175$  s. (b)  $I_{\text{in}}=266$  mW,  $T_{\text{acc}}=150$  s. (c)  $I_{\text{in}}=410$  mW,  $T_{\text{acc}}=140$  s. (d)  $I_{\text{in}}=83$  mW,  $T_{\text{acc}}=150$  s. The energy resolution for each spectrum is indicated on the left.

*et al.*<sup>8</sup> We can calculate the absolute Raman scattering cross section from the measured absolute intensity using Eq. (3).

#### IV. RESULTS

For samples *B* and *C* no Raman peak for the stretching vibration of monohydride, dihydride, and trihydride was observed. For sample *A* a Raman peak was clearly observed at  $\sim 2085$   $\text{cm}^{-1}$ , as shown in Fig. 1. The Raman spectra in Fig. 1 are uncorrected bare data. The peak at  $\sim 2085$   $\text{cm}^{-1}$  is assigned to the in-phase terrace vibration of monohydrides on Si(111).<sup>8</sup> The results from MIRAS (Ref. 20) show that the natural linewidth of this terrace mode is inherently less than 1  $\text{cm}^{-1}$  at room temperature. The observed linewidth of the peak in Fig. 1 agrees with the instrumental resolution that is determined by the slit width of the monochromator. For sample *A* no stretching vibration modes (2106–2140  $\text{cm}^{-1}$ ) assigned to the dihydride and trihydride vibrations were observed.

Figure 2 shows the incident wavelength dependence of the absolute Raman scattering cross section of the Si-H terrace mode. The open circles are the data points. The error bars are estimated from the statistical fluctuation  $\sqrt{N}$  of the Raman peak photon number  $N$ . The solid curve is the calculated  $\omega^4$  dependence. It is fitted to the data points by the method of least squares. The data points agree very well with the  $\omega^4$  curve. From this fitting, the absolute Raman scattering cross section of the terrace vibration mode at the incident wavelength of 4800 Å is

$$\left(\frac{d\sigma_{zz}}{d\Omega}\right) = (8.37 \pm 0.32) \times 10^{-28} \text{ cm}^{-2}/(\text{sr line Si-H bond}), \quad (6)$$

where  $\pm 0.32$  is the uncertainty determined by the mean-square fitting.

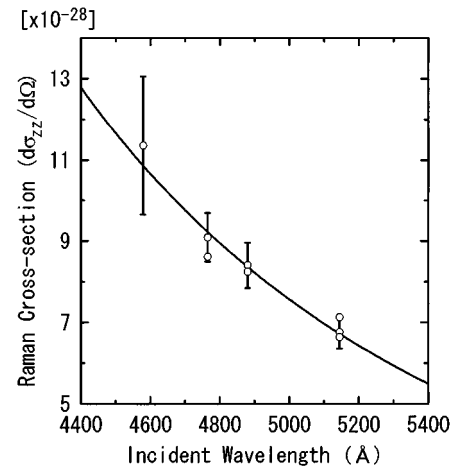


FIG. 2. Absolute Raman cross section of the Si-H terrace vibration mode as a function of the wavelength of the incident light. The open circles are the experimental data points. The solid curve is a root-mean-squared fit to a  $\omega^4$  curve. The unit of the absolute Raman cross section, corresponding to the vertical axis, is  $\text{cm}^2/(\text{sr line Si-H bond})$ .

#### V. DISCUSSION

The absolute Raman scattering cross section of the terrace vibration of monohydrides on Si(111) that we obtained above is greater than most of the known absolute cross sections of gaseous molecules.<sup>21</sup> For example, it is interesting to compare the present result with the Raman cross section of the symmetric stretching vibration ( $\nu_1$ , 2185.7  $\text{cm}^{-1}$ ) of the  $\text{SiH}_4$  molecule in the gaseous state:

$$\left(\frac{d\sigma}{d\Omega}\right) = 1.13 \times 10^{-29} \text{ cm}^2/(\text{sr molecule}); \quad (7)$$

that is, the quantum cross section derived from the power cross-section at the incident wavelength of 4880 Å in Ref. 22. Although we are looking at the same stretching vibration of the Si-H bond, the cross section of the Si-H terrace mode is about 74 times greater than that of the Si-H stretching mode of  $\text{SiH}_4$ .

Now let us consider the mechanisms that can possibly cause the observed difference between the cross sections of the Si-H terrace mode and the stretching mode of  $\text{SiH}_4$ . Possible candidate mechanisms that we have considered are (1) enhancement of the local electric field due to surface roughness (similar to SERS), (2) resonance due to electronic transitions, and (3) larger dipole transition matrix elements.

On rough surfaces or island films of metals, especially of silver, surface plasmons (SP's) are resonantly excited by the incident light and the excitation of the SP's enhances the local electric field at the site of the adsorbed molecule.<sup>1,23</sup> This enhancement effect is believed to be operative in SERS,<sup>1</sup> but the presence of surface roughness is essential for this mechanism to be effective. In the case of semiconductor surfaces, the SERS enhancement mechanism is weak in comparison with the metallic case. For fine GaP particles with diameters of 400–1000 Å, the enhancement factor of a few hundred<sup>11</sup> has been reported. The surface of sample *A* in the present study is extremely smooth, and the necessary rough-

ness does not exist on the surface. Hence the enhancement of the Raman intensity due to the resonant excitation of SP's cannot be expected. This conclusion is supported by the result that no Raman peak in samples *B* and *C* was observed, although the surface roughness of samples *B* and *C* is greater than that of sample *A*.

When the energy of the incident and/or scattered light lies close to the energy of the electronic transitions of the adsorbed molecules, the Raman scattering cross section is enhanced due to resonance.<sup>24</sup> The energy levels of the monohydride on Si(111) have been investigated by ultraviolet photoemission spectroscopy (UPS) measurements and theoretical calculations.<sup>25–27</sup> Their results show that for the monohydride the highest filled state is located about 4.5 eV below the Fermi level, and the lowest empty state is located about 3 eV above the Fermi level. Thus the absorption due to the optical transitions of the Si-H bond is expected to have a peak in the range of 7–8 eV.<sup>27</sup> Since the energy of the incident photons in the present Raman study is much smaller than that of this optical transition, the enhancement of the Raman intensity by resonance cannot be expected. The experimental result shown in Fig. 2 also confirms this conclusion. The excitation profile of the Raman scattering cross section in Fig. 2 shows a  $\omega^4$  dependence without any indication of electronic resonances.

From the above considerations we see that the first two enhancement mechanisms of the Raman scattering cross section are not operative in the present situation. Thus we must conclude that the dipole matrix elements that enter the Raman cross section for the Si(111)/H system is larger than those for the free SiH<sub>4</sub> molecule. This means that the electronic wave function of the Si-H bond in the Si(111)/H system is significantly different from that found in the SiH<sub>4</sub> molecule. The expression for the Raman polarizability consists of the sum of terms that contain two dipole transition matrix elements in the numerator. Hence, roughly speaking, the Raman polarizability is proportional to the square of typi-

cal dipole matrix elements, and the Raman cross section in turn is proportional to the fourth power of the dipole matrix elements. To account for a factor of about 80 in the Raman cross section, one needs a factor of 3 in the size of the dipole matrix elements. A change in the size of dipole matrix elements of a factor of 3 due to the difference in the nature of the bonds between the Si(111)/H system and the free SiH<sub>4</sub> molecule seems to lie within a reasonable range. To understand the difference in detail, it is necessary to perform a theoretical calculation of the Raman polarizability for the two systems.

## VI. CONCLUSION

We have measured the absolute Raman scattering cross section of the Si-H terrace vibration mode on Si(111). The cross section is larger than most of the cross sections of free gaseous molecules, and is about 74 times that of the symmetric stretching vibration of SiH<sub>4</sub>. The usual enhancement mechanisms of Raman cross sections, such as enhanced local electric fields due to surface roughness and electronic resonances, cannot explain the large difference in the cross sections between the monolayer of Si-H on Si(111) and the free SiH<sub>4</sub> molecules. At present, we conclude that the relevant electronic wave functions of the Si-H monolayer is significantly different from those of the free SiH<sub>4</sub> molecule. We estimate that the Raman transition dipole matrix elements are about three times larger for the Si(111)/H monolayer system than for the free SiH<sub>4</sub> molecule.

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